

**P-037: A study of the decomposition products of furfural, xylose and isophorone using NMR**Gerardo Gomez Millan<sup>1,2</sup>, Alistair W. T. King<sup>3</sup>, Jordi Llorca<sup>1</sup>, Herbert Sixta<sup>2</sup><sup>1</sup>*Department of Chemical Engineering, Institute of Energy Technologies and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain*<sup>2</sup>*Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo, Finland*<sup>3</sup>*Materials Chemistry Division, Chemistry Department, University of Helsinki, Helsinki, Finland*  
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In recent years we have witness lots of activity to upgrade sugars contained in lignocellulosic biomass into ethanol and other value-added chemicals. An interesting catalytic route, namely the dehydration of sugars (pentoses and hexoses found in lignocellulose) to furans, is considered one of the most promising routes for the production of platform chemicals and fuels [1]. One attractive furanic compound, furfural (FUR), has been identified as a direct or indirect feedstock to more than 80 chemicals [2,3]. The current FUR production uses mineral acids at approximately 200 °C, providing around 50 mol% yield [4]. Low yields in this process are mainly due to FUR decomposition with other compounds via resinification and condensation producing insoluble polymers (humins) [5]. A practical way to inhibit the formation of humins is to extract the FUR instantaneously from the aqueous solution into an organic phase [6].

In this study, the production of FUR from xylose was carried out using a biphasic batch reaction system. Isophorone and cyclopentyl methyl ether (CPME) were used to extract FUR from the aqueous phase to enhance the overall FUR yield by limiting its degradation. Due to their water-immiscibility nature, these organic solvents do not require salt addition, which is a significant advantage over other water-miscible organic solvents. The effect of time, temperature and organic-to-aqueous ratio on xylose conversion and FUR yield were investigated. Experiments conducted at three temperatures (170, 190 and 210 °C) were studied in a stirred microwave-assisted batch reactor, which established the optimal conditions to obtain the highest FUR yield. The maximum FUR yields obtained from xylose were 78 mol% when using CPME and 48 mol% when using isophorone with an aqueous to organic phase ratio of 1:1.

In the present work from isophorone and CPME, the latter demonstrates a higher selectivity towards FUR (and thus higher FUR yield) without decomposition. This suggests that FUR undergoes decomposition reactions, potentially including isophorone as a co-reactant. Alternatively, the rate of degradation of FUR may be increased by an increasing content of water at temperatures approaching 200 °C. These possibilities were investigated by NMR analysis of the degradation of FUR: isophorone molar ratios of 1:1 and 1:10 at 190 °C over 30 min (Figure 1). Potential mechanisms for this degradation might be, for example, Diels-Alder cycloaddition (isophorone as hindered dienophile), Aldol condensation (isophorone C6 reacting as nucleophile at the FUR aldehyde), Baylis-Hillman reaction (isophorone C2 reacting as nucleophile at the FUR aldehyde) and Michael addition (isophorone C3 as  $\alpha$ - $\beta$  unsaturated electrophile). Other reactivity may of course be possible [7,8,9].

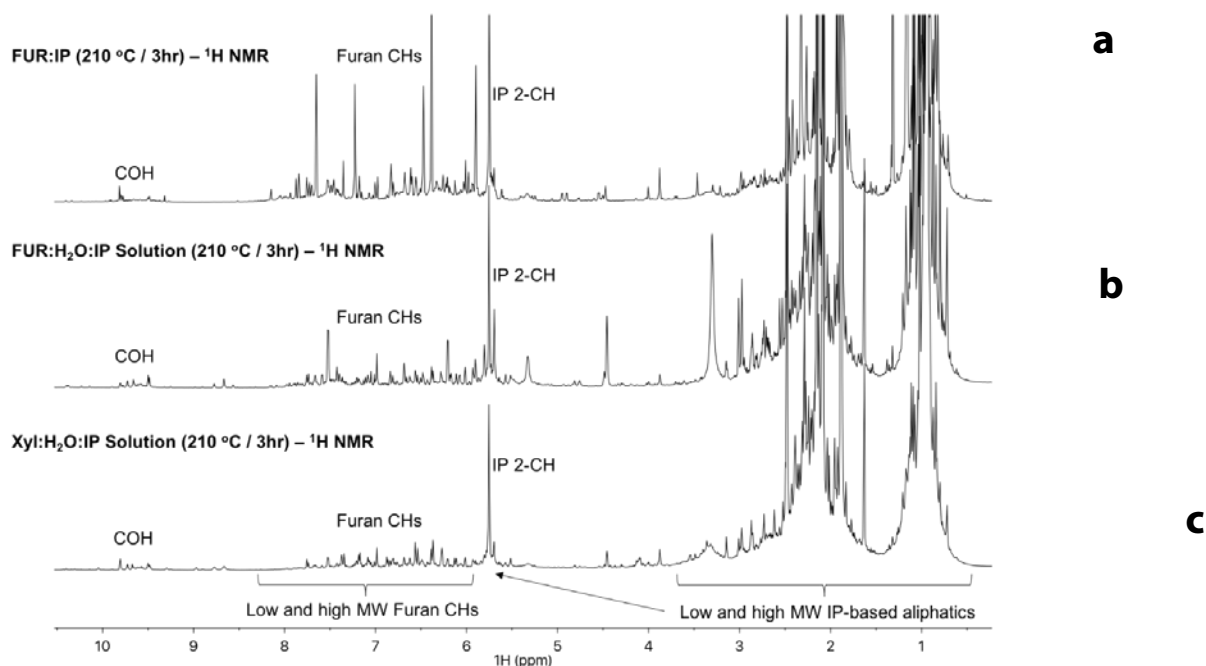


Figure 1.  $^1\text{H}$  NMR spectra (DMSO- $d_6$  at 27 °C) of 1:10 molar equivalents of FUR:isophorone heated at 190 °C for 30 and 120 min.

## References

- [1] BOZELL, J.J., and G.R. PETERSEN, 2010: *Green Chem.*, **12**, 539-554.
- [2] MARISCAL, R., MAIRELES-TORRES, P., OJEDA, M., SADABA, I., and M. LOPEZ GRANADOS, 2016: *Energy Environ. Sci.*, **9**, 1144-1189.
- [3] KAMM, B., GRUBER, P.R., and M. KAMM, 2010: Wiley-VCH.
- [4] ZEITSCH, K.J., 2000: *Sugar Series.*, **13**, 1-2.
- [5] VAN ZANDVOORT, I., WANG, Y., RASRENDRA, C.B., VAN ECK, E.R.H., BRUIJNINCX, P.C.A., HEERES, H.J., and B.M. WECKHUYSEN, 2013: *ChemSusChem.*, **6**, 1745-1758.
- [6] WEINGARTEN, R., TOMPSETT, G.A., CONNER JR., W.C., and G.W. HUBER, 2011: *Journal of Catalysis*, **279**, 174-182.
- [7] THIYAGARAJAN, S., GENUINO, H.C., SLIWA, M., VAN DER WAAL, J.C., DE JONG, E., VAN HAVEREN, J., WECKHUYSEN, B.M., BRUIJNINCX, P.C.A., and D.S. VAN ES, 2015: *ChemSusChem.*, **8**, 3052-3056.
- [8] SHANMUGAM, T., GENUINO, H.C., VAN DER WAAL, J.C., DE JONG, E., WECKHUYSEN, B.M., VAN HAVEREN, J., BRUIJNINCX, P.C., and D.S. VAN ES, 2016: *Angew. Chem. Int. Ed.*, **55**, 1368-1371.
- [9] GENUINO, H.C., SHANMUGAM, T., VAN DER WAAL, J.C., DEJONG, E., VAN HAVEREN, J., VAN ES, D.S., WECKHUYSEN, B.M., and P.C. BRUIJNINCX, 2017: *ChemSusChem.*, **10**, 277-286.